

Ground state measurement of Pr^{3+} in Y_2O_3 by photoconductivity

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1 at.% Pr^{3+} doped Y_2O_3 single crystal fiber is prepared using a laser heated pedestal growth method. Emission and excitation spectra of the fiber have been measured. The emissions of 1D_2 to 3H_4 and 1D_2 to 3H_5 $4f-4f$ transitions are found at 620 and 720 nm, respectively. The 3P_2 , 3P_1 , 1I_6 and 3P_0 , $4f-4f$ absorptions are observed at 456, 472, 482 and 492 nm respectively. The $4f-5d$ absorption band is detected at 288 nm. Photoconductivity result shows that the $4f-5d$ transition of Pr^{3+} produces a direct photocurrent around 285 nm. Taking the onset photocurrent at 320 nm, the ground state of Pr^{3+} is determined at 1.7 eV above the valence band of the host.

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1. Introduction

Trivalent rare earth (RE^{3+}) ions are important for various applications, such as lamp phosphors and information display materials [1–3]. Recently, some research work on RE^{3+} doped luminescence materials has been to study the delocalization of excited state electrons [4]. Excitation state electron delocalization is one of the major problems that may cause quenching of luminescence and laser action [5,6]. In general, such a delocalization happens to the d electrons rather than f electrons because the d state of the dopants usually overlap the conduction band of the hosts, which creates a physical path for delocalization [7]. Therefore, the excited state structure of the RE^{3+} ions relative to the host band gap becomes the key factor that determines the delocalization of electrons.

Theoretical predictions of the band structure relative to the host band gap have been carried out in many hosts for RE^{3+} and RE^{2+} ions [8]. But these predictions yield also some incorrect information [9–11]. Thus experimental determinations of the band structures are needed. The first set of band structure of RE^{3+} in yttrium aluminum garnet (YAG) host was determined and estimated using a photoemission method [12,13]. The results revealed that the $5d$ states of the ions are close to host conduction band and the $4f$ ground states are close to the host valence band.

In this work, the band structure of the Pr^{3+} ions relative to Y_2O_3 host is determined using a photoconductivity measurement. It is a following effort in determining the band structures of the RE^{3+} in Y_2O_3 . Using the photoconductivity method, the ground states of Ce^{3+} , Tb^{3+}

and Er^{3+} ions have been found to be 2.8, 1.3 and -1.0 eV respect to the host valence band [14–16].

Pr^{3+} is the ion next to Ce^{3+} with two valence electrons. Both $4f-4f$ and $4f-5d$ transitions exist in Pr^{3+} doped materials. The competition of $5d$ state and 1S_0 state of Pr^{3+} in strontium aluminates is of interest in quantum cutting phosphors [17,18]. Pr^{3+} has also important applications in long persistent phosphors and light emitting diode phosphors (LED). In these cases, photoionization of excited state electrons are important to the performance of these phosphors, so that the band structure will provide information to the applications [19,20].

2. Experimental

The $\text{Y}_2\text{O}_3:\text{Pr}^{3+}$ single crystal fibers have been prepared using a laser heated pedestal growth (LHPG) method [15,21]. Y_2O_3 and $\text{Pr}(\text{NO}_3)_3$ powder mixtures were made with a proper mole ration (1% doping concentration) and were heat-treated at 900°C for 2 h. The treated raw materials were re-mixed, pressed into pellets and sintered at 1200°C in air in a Linderburg blue tube furnace for 2 h. The sintered pellets were cut and polished into 1×1 mm square rods for laser pulling. The single crystal fibers were reduced at 1350°C in a 5% $\text{H}_2 + 95\%$ N_2 gas flow in order to obtain Pr^{3+} . The fiber samples were polished into $300\ \mu\text{m}$ thin slabs along their fiber axis with two parallel side surfaces.

Photoconductivity spectra of the samples were measured at room temperature. Ni meshes were used to serve as the electrodes. The light source for excitation was an Oriel 200 W xenon lamp filtered through an ISA Jobin Yvon Spex

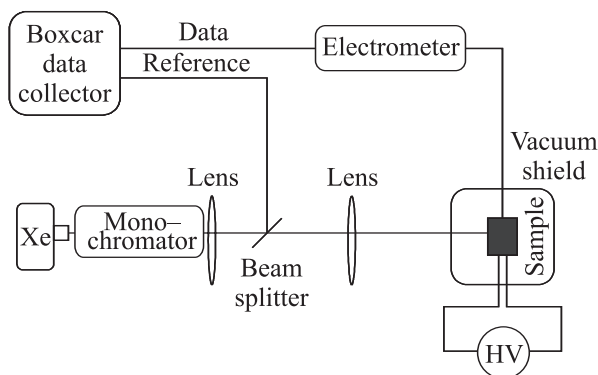


Figure 1. Experimental setup for the photoconductivity measurement.

monochromator. The light was split into two using a beam splitter. One beam was directed to a Box Car data collector as reference, the other was focused onto the sample. The sample was mounted in a thermally and electrically shielded vacuum chamber ($< 10^{-5}$ Torr) with a 10 000 V/cm voltage, applied across the two ends. A Keithley 6517A electrometer was used both as a high voltage supply and as a current detector. Emission and excitation spectra were collected by a SPEX FluoroMax II spectrometer. A schematic diagram for the experimental setup is presented in Fig. 1.

3. Results and discussion

Emission (dotted line) and excitation (solid line) spectra of 1% Pr^{3+} in Y_2O_3 are shown in Fig. 2. The Pr^{3+} emission bands of the $4f-4f$ transitions from 1D_2 to 3H_4 and 3H_5 states are found around 620 and 720 nm, respectively. The Pr^{3+} 3P_2 , 1I_6 , 3P_0 excitation peaks of the $4f-4f$ absorptions are observed at 456, 472, 482, and 492 nm, respectively [22,23]. The $4f-5d$ absorption band of Pr^{3+} is detected at 288 nm. This value is corrected from Ref. [22] that recorded at 300 nm.

The photocurrent spectrum measured with the lamp power of 60 W is depicted in Fig. 3. The photocurrent starts to rise rapidly at about 220 nm which is consistent with the 5.6 eV band gap energy of the Y_2O_3 host. Another photocurrent peak is detected at 285 nm that has slightly higher energy position compared to the $4f-5d$ excitation peak, indicated as a reference in the figure at 288 nm. This suggests that the bottom of the conduction band to the ground state of Pr^{3+} is slightly higher than the lowest position of the $5d$ states to the ground state of Pr^{3+} , requiring higher energy than $4f-5d$ transition to photoionize the ions to generate photocurrent. In this system, the major part of the $5d$ states of Pr^{3+} overlaps with the conduction band.

To further investigate the photocurrent at 285 nm the photocurrent spectra were measured with different excitation light intensity, controlled by adjusting the lamp output power from 40 to 160 W. The photocurrent intensity

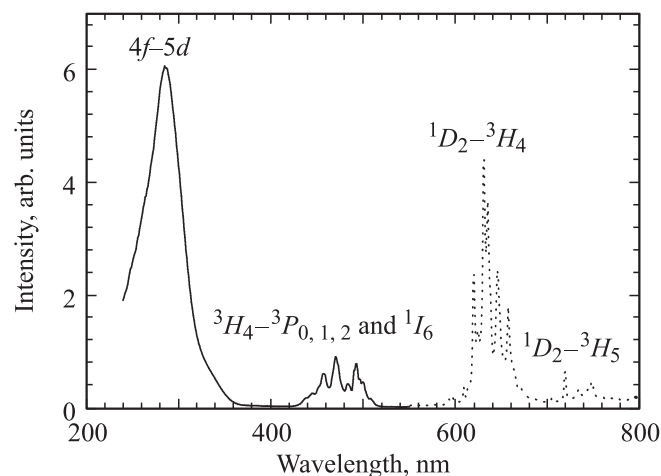


Figure 2. Emission (dotted) and excitation (solid) spectra of $\text{Y}_2\text{O}_3:\text{Pr}^{3+}$.

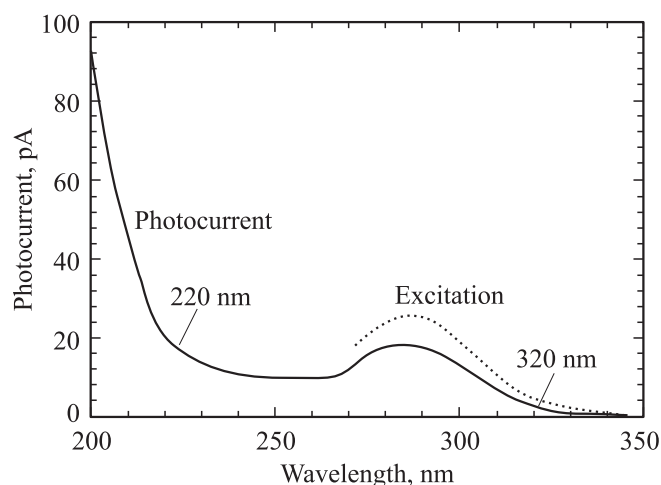


Figure 3. Photoconductivity spectrum of $\text{Y}_2\text{O}_3:\text{Pr}^{3+}$. As comparison, excitation peak of Pr^{3+} $4f-5d$ transition is added (dashed line).

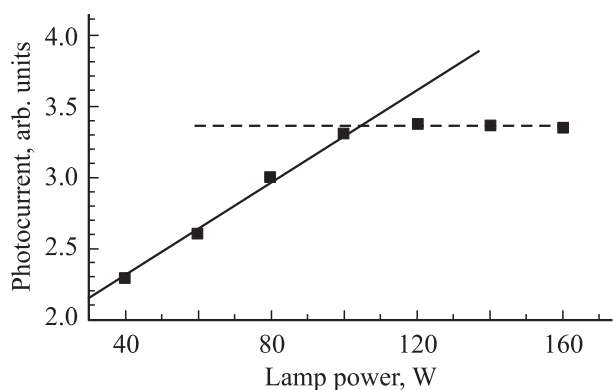


Figure 4. Photocurrent dependence on the excitation power.

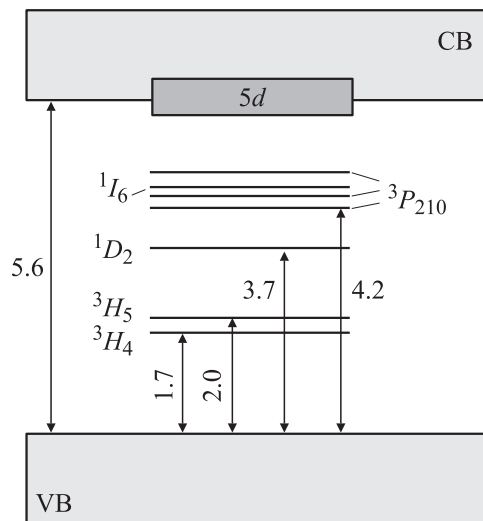


Figure 5. Pr^{3+} energy structure (in eV) relative to the Y_2O_3 band gap.

at 285 nm is observed linearly dependent to the lamp power up to 100 W, as shown in Fig. 4. The photocurrent starts becomes flat at higher powers, indicating a saturated absorption. The linear dependence at lower powers shows the photocurrent as a single photon process.

Based on above information, it is found that the lowest state of the $5d$ band is just below the conduction band. Taking the onset photocurrent at 320 nm, as indicated in Fig. 3, the ground state is about 3.9 eV below the host conduction band. The band gap energy is 5.6 eV so that the ground state of Pr^{3+} lies 1.7 eV above the valence band. In such case the 288 nm $5d$ peak is about 0.5 eV above the bottom of the conduction band. Considering the temperature dependence, i.e. the thermal ionization of $5d$ electrons, the actual value may have a ± 0.2 eV error. The rest of the energy levels of Pr^{3+} can be readily located in the band gap with these two band positions fixed in respect to the band gap, as illustrated in Fig. 5. The unit for all the numbers in the figure is eV.

4. Conclusions

In summary, single crystal fiber of $\text{Y}_2\text{O}_3:\text{Pr}^{3+}$ was prepared using a LHPG method. Emission and excitation spectra and photoconductivity are measured. The ground state position of Pr^{3+} in Y_2O_3 is determined to be 1.7 eV above the host valence band.

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